SELECTIVE MONITORING OF TRITIUM-CONTAINING SPECIES IN A GAS

The present invention is concerned with a method and apparatus for selectively monitoring hydrophilic tritium-containing species in a gas, and in particular with such a method and apparatus which selectively monitors hydrophilic tritium-containing species in the air of a controlled area for tritium handling.

Tritium is an isotope of hydrogen which undergoes radioactive decay by emission of a beta-particle. The most common forms of tritium encountered in air are the elemental forms HT, DT or T2 (usually referred to generically as HT) and the oxidised forms HTO, DTO and T2O (usually referred to generically as HTO). The elemental form of tritium has a radiotoxicity 25000 times lower than the oxidised form, according to the International Commission on Radiation Protection. This is because, whereas the oxidized form mixes thoroughly with water in the lungs, the elemental form is hardly absorbed at all and shows a slow rate of isotope exchange with water in the body. It is also thought that the absorption of HT has been somewhat underestimated, so that a HTO/HT radiotoxicity ratio of as low as 1000 may be more appropriate.

Other tritiated molecules, such as tritiated hydrocarbons, methanol etc., can often be present in the gas. The radiotoxicities of these species depends on the extent to which they enter, or exchange tritium with, water in the lungs.

Clearly it is important to distinguish between the chemical forms of tritium, especially between the most common forms; oxidized and elemental; because of the large difference in radiotoxicity.

Presently tritium is monitored either without discriminating between the aforementioned two main chemical forms, by, for example, using ionisation chambers, internal gas-proportional counters or the like, or using scintillators of various kinds, such as, for example, anthracene, or the like. Other means include delayed methods that separate the humidity from the air, for example, by absorption in a bubbler, desiccation, condensation or freezing. The sample must then be measured by, for example, liquid scintillation counting or alternatively by one of the above identified methods.

Monitoring and measurement of tritium concentration in ambient air, is generally carried out using monitors such as ionisation chambers.

One type of monitor, selective for tritiated water, which has been previously used is generally based on two ionisation chambers connected by a selectively permeable (Nafion-Dupont) membrane. Such a monitor has been developed so as to discriminate between HTO and HT concentrations in a gas. Monitors of this type generally suffer from the disadvantage that they have a limited discrimination factor due to the permeability of the membrane for both HTO and HT. Furthermore, they can take long periods of time to perform the necessary measurements due to the time-period which is sufficient for the gas to penetrate the membrane. Such systems are also typically bulky and expensive.

Another type of HTO-selective monitor consists of two ionization chambers in series, separated by a drier. The HTO concentration is deduced by subtracting the signal emitted by the second ionization chamber from that of the first ionization chamber. A disadvantage

of this type of system is that, if HT is present in higher concentrations than HTO, the errors in the ionization chamber measurements may greatly exceed the HTO concentration. The system is also bulky and expensive.

It is an object of the present invention to alleviate such disadvantages, and additionally to provide a novel method and apparatus which can discriminate between the oxidised and elemental forms of tritium in a gas.

Therefore, according to a first aspect of the present invention there is provided a hygroscopic scintillator, suitable for selective response to tritiated water vapour and other hydrophilic tritiated species in a gas, which scintillator comprises a solid scintillator material having a layer of hygroscopic material thereon. Such a scintillator advantageously allows tritiated water vapour or other hydrophilic gas species, such as, for example, tritiated ammonia, tritiated methanol or the like to enter or exchange tritium, holding the tritium from said species in close proximity to the surface of the solid scintillator material.

The range of beta-emission from tritium (average about 0.4 microns in liquid water) allows the tritium in the hygroscopic layer to excite the solid scintillator component of the hygroscopic scintillator element. Advantageously, the hygroscopic material may comprise a layer of any hygroscopic or deliquescent substance such as a solution of deliquescent compound, or an aqueous gel of said compound. In one embodiment a hydrated solid or zeolite may be used which has the advantage that for some desired applications they are selective only for tritiated water, and not other

hydrophilic species.

The range of tritium beta-emissions being limited, only the surface region of the scintillator material of the scintillator element contributes to the monitor sensitivity. Therefore said scintillator material may advantageously be provided in a form which comprises a high specific surface area, for example as a sheet, as fibres, powder, powder compact, paint, varnish or a combination of the said forms.

There is provided by a second aspect of the present invention a method of monitoring tritiated water vapour or other tritiated species activity in a gas, which method comprises contacting said gas with a scintillator according to the invention, said scintillator being enclosed in a substantially light tight container, and measuring the light emitted from said hygroscopic scintillator, the amount of said emitted light providing a measure of the tritiated activity of said gas.

The method according to this aspect of the present invention advantageously discriminates between the oxidised form of tritium in a gas, and the elemental form of tritium, the oxidised form of tritium being highly radio-toxic compared to the elemental form.

Furthermore, during operation the hygroscopic scintillator element contains an amount of HTO typically contained in a volume of gas much larger than the volume of the element. Therefore, the method according to the first aspect of the present invention advantageously allows a much more compact format than an ionization chamber sensitive to the same activity of HTO in gas.

Advantageously, the method according to this aspect of the present invention may have a sensitivity to all tritium-containing species in the gas, substantially in proportion to the amount in which they enter or exchange tritium with the water-containing layer in the hygroscopic scintillating element. Since the relative radiotoxicity of the tritiated species depends substantially on their entry and isotope-exchange with water in the human lung, the method provides a good indication of the overall radiotoxicity of the gas mixture due to all tritium species present.

Solid scintillators advantageously emit light when subjected to beta-emissions from tritium, and, unlike liquid scintillation cocktails, have a stable geometrical form and negligible evaporation rates. Preferably, the scintillator according to the invention may be, for example, a plastic, a glass, an inorganic "phosphor" (e.g. doped zinc sulphide), an oxide-based material (e.g. Yttrium Aluminium Garnet "YAG" or Yttrium Aluminium Perovskite "YAP": crystalline oxides available in transparent single crystal form), or a combination of these materials, none of which absorb significant quantities of water.

Advantageously, to improve wetting, the solid scintillator material may be pre-treated on the surface with a detergent, or subjected to a hydrophilic surface treatment such as sulfonation or the like; or alternatively detergent may added to the aqueous component.

Preferably, a light guide may be provided to help transmit light from the scintillator to the light detector(s). In some cases, the solid scintillator material itself may act as a light guide. Preferably,

where the detectors are, for example, remote from said scintillator element and outside any light tight container, the light guide may be of a material which prevents entry or exit of any light.

When measuring tritiated activity in a process gas, such as, air, the humidity of the air can affect the reading in two ways. Firstly, for a given activity of tritiated water, for example, in the gas (in terms of Becquerel per cubic meter of gas), the concentration of tritium per gram of water is inversely proportional to the humidity of the gas. This effect tends to decrease the sensitivity of the monitor (in terms of Becquerel per cubic meter of gas) as the humidity increases. Secondly, the amount of water present in the hydrated layer increases with the humidity, depending on the absorption characteristics of the hygroscopic material. This in turn tends to increase the amount of water contributing to the scintillation, and hence tends to increase the output of the monitor as humidity increases. Therefore, the two effects tend to cancel each other. Preferably, by optimizing the nature and thickness of the layer of hygroscopic material, the variation in sensitivity of the output with changing humidity in the gas can be minimized.

In a preferred embodiment of this aspect of the present invention, the light emitted by the hygroscopic scintillator element is measured by one or more light detectors which include photomultipliers, multichannel plates, or photodiodes or the like which would be well known to those skilled in the art. The electronics associated with such light detectors may use conventional current-pulse-counting, each pulse corresponding substantially to a light pulse from a scintillation event. As is usual for scintillation techniques, the rate of current pulses is

substantially proportional to the rate of scintillation events. Where two or more light detectors are used, one may advantageously reduce noise background by well-known pulse coincidence detection techniques. If the light output is sufficient, continuous average-current monitoring may be used instead of pulse counting.

In one embodiment of this aspect of the present invention the gas to be monitored may be air. Thus, advantageously, the method may be used to monitor tritium intake, for example, by radiation workers in a controlled handling area. In a preferred embodiment the air tritium monitor may be small enough to be portable which may therefore allow it to be carried continuously by workers in a controlled area.

In another embodiment of this aspect of the present invention, the gas to be monitored may be enclosed in a chemical plant: an application normally described as a "process monitor". In a light-tight plant, the monitor may be inserted through the plant wall (for example into a pipe or storage tank) without the need for its own light-tight container.

Preferably, such a process monitor may be used in conjunction with a non-discriminating monitor in order to measure, by difference, the concentrations in gas or air of both tritiated water (possibly together with hydrophilic species) and elemental tritium (possibly together with other hydrophobic species). In this embodiment, the non-discriminating tritium monitor may be substantially identical to the discriminating monitor comprising a scintillator element according to the invention with the exception that the hygroscopic layer is omitted in the non-discriminating monitor.

Preferably, a second radiation monitor; preferably substantially identical to the said discriminating monitor, but sealed in a container free of radioactive gas, may be provided to compensate for background radiation fields (e.g. gamma-radiation), by subtraction: an analogous technique is already used for compensating ionization chambers for radiation background.

According to a further aspect of the invention there is provided apparatus for monitoring the level of tritiated water and other tritiated hydrophilic species in a gas, which apparatus comprises, a hygroscopic scintillator according to the invention, and means for measuring the amount of light emitted from said hygroscopic scintillator element. In one embodiment of this aspect of the invention, means may be provided for contacting said gas with said hygroscopic scintillator. The measuring means may either be connected to said hygroscopic scintillator element or may be provided remotely from it by means of a light guide.

Thus, advantageously, the apparatus according to this aspect of the invention allows for a measure of the level of tritium in a gas, such as air, to be provided. The apparatus responds with much greater sensitivity to tritiated species, such as tritiated water vapour, which are more radiotoxic because they mix or exchange hydrogen isotopes rapidly with water.

This further aspect of the present invention may be provided in the form of a stand-alone room air monitor, a personal tritium monitor or an "in-line" process gas monitor for mounting with tube connectors in the pipework of a chemical process using tritiated gas.

In one embodim nt of this aspect of the invention the hygroscopic scintillator may be enclosed in a substantially light-tight container with a window(s) or aperture(s) being provided therein to allow emitted light to reach the light detector(s), in addition to an inlet adapted to allow access of said gas to the hygroscopic scintillator element but to prevent light escaping from or entering said container. An outlet may also be provided to allow flow of said gas over or through the hygroscopic scintillator element from said inlet to said outlet. Preferably, said inlet and outlet minimize the entry of external light by, for example, the use of dark or black materials and which may have a geometry which forces the light to make multiple reflections before reaching the monitor.

For a stand-alone room air monitor, a pump may preferably be provided to pass air continuously through the monitor. Furthermore, a dust filter may be mounted at the inlet. When the apparatus is used as a personal tritium monitor, a pump may be provided, or alternatively the monitor may be built into a breathing mask so that the flow of air is provided by the breathing of the worker. Furthermore, when used as a process gas monitor, a pump may be used to pass gas therethrough if the gas flow or pressure drop available inside the plant is insufficient. Such an application could be, for example, the monitoring of tritium in an inert-gas glovebox. The pump may be of many types, for example, including a membrane pump, an electrical fan or impeller, a centrifugal pump or advantageously (for reason of low power consumption) a piezo-electric fan built into a housing. Thus advantageously the apparatus according to the invention may provide a substantially continuous and accurate monitoring of the tritium radiotoxicity in a gas.

The apparatus in an alternative embodiment may also be provided in the form of a "nude" monitor for process gas in an existing light-tight tank or pipe. Lacking its own light-tight casing, the apparatus according to the invention may be fixed to an aperture in the plant wall or pipe with a substantially light-tight seal. In this embodiment, gas flow through or over the hygroscopic scintillator element may be provided by the existing flows inside the plant, or alternatively by a fan.

Advantageously, the apparatus according to the present invention uses a hygroscopic material coated onto a solid scintillator to make a hygroscopic scintillating element. Said hygroscopic layer may consist of a layer of a hygroscopic or deliquescent substance such as a solution of deliquescent compound, or an aqueous gel of said compound. Many compounds are suitable examples included but are not limited to zinc chloride, potassium acetate, phosphoric acid, lithium chloride. Alternative types of hygroscopic layers could consist of a hygroscopic organic solid or liquid, for example, poly-(ethylene oxide), a soap, sugar, polyhydroxymethylemethacrylate or a glycol. The use of a gel containing deliquescent compound may advantageously impede long-term redistribution of the hygroscopic layer across the surface. A hydrated solid such as, for example, zeolite may also be used in said hygroscopic layer. Although having a relatively slow exchange rate of water with the water vapour in the gas, this embodiment has the advantage in some special applications of being selective only for tritiated water, and not other hydrophilic species.

The solid scintillator material, or a combination of solid scintillator materials, may advantageously be

applied as a paint (e.g. zinc sulphide paint) or varnish (e.g. plastic scintillator dissolved in organic solvent, possibly mixed with YAP powder) to the surface of the light guide. The advantages are a reduction in cost of scintillator material, efficient light collection, and relative insensitivity to gamma radiation, due to the small mass of solid scintillator present. In other foreseen designs the solid scintillator may function as a light guide.

In the apparatus according to the invention, the inner walls of the light-tight container, or the surface of a light guide, may preferably be made reflective, for example by polishing or aluminizing, to improve light collection efficiency.

The apparatus according to the invention has a certain sensitivity to HT and other hydrophobic tritiated species due to the arrival at the scintillator of tritium beta emissions arising from such species in the gas in and around the scintillator element, the range of tritium emissions in gas being much greater than in condensed phases. This sensitivity to HT is approximately proportional to the volume of gas in and around the scintillator element. It is possible to vary the relative sensitivity to HT, for a given HTO sensitivity, by keeping the same surface area and preparation method for the hygroscopic scintillator element, but varying its overall size to change the gas space inside the scintillating element. Alternatively, extra scintillator material may be added which is not covered by a hygroscopic layer. Thus the ratio of HTO to HT sensitivity may be adjusted to match a desired value, for example 1000.

Preferably, the measuring means for measuring light emitted by the hygroscopic scintillator element

comprises one or more light detectors, including photomultipliers, multichannel plates with photodiode detectors, or photodiodes. The electronics associated with such light detectors may use conventional current-pulse-counting, each pulse substantially corresponding to light pulse from a scintillation event. As usual for scintillation techniques, the rate of current pulses is substantially proportional to the rate of scintillation events. Where two or more light detectors are used, one may advantageously reduce noise background by well-known pulse coincidence detection techniques. If the light output is sufficient, continuous average-current monitoring may be used instead of pulse counting.

Preferably, electronics are provided to convert the rate of charge pulses or average current into a signal which is substantially proportional to the radiotoxicity of the gas, or its logarithm. Said signal may preferably be displayed on a meter or digital display and/or converted to an audible signal, and/or made available as an output to a computer, data-logger or other external recording or control apparatus. A standard humidity gauge may be incorporated into the monitor, or a separate humidity gauge may be read into said recording and control apparatus, in order to allow automated or manual compensation for the effects of gas or air humidity on the sensitivity of the present tritium monitor or apparatus according to the invention. Furthermore, it is foreseen that the function of said humidity gauge may be incorporated into the monitor by measuring the electrical AC or DC conductivity of the hygroscopic layer, for example by measuring the resistance between two metallic contacts applied to the surface of the solid scintillator before coating with the hygroscopic layer.

The invention may be more clearly understood by the following description of an embodiment thereof, with reference to the accompanying drawing given by way of example only, wherein

Figure 1 is an illustration of apparatus for monitoring the tritiated water content, or more generally, radiotoxicity of a gas containing tritium species, according to the invention.

Figures 2 to 6 illustrate alternative embodiments of the apparatus of Figure 1. In each figure there is shown one or more light detectors, and a hygroscopic scintillator element. Some designs have a light guide incorporated therein.

Referring to the drawings and initially to Figure 1, there is shown a simple design for a hygroscopic scintillator element according to the invention incorporated into a monitor 1. In use the monitor functions when gas 2 passes over one surface of a flat hygroscopic scintillator element 3, which can be supported by a backing plate 14. In this embodiment no light guide is provided and the scintillation light pulses emitted from the element 3 pass through the sample gas 2 to reach the light detector 4. This design is particularly suitable for fragile scintillator elements: powder compacts and the like and for layers of substantially opaque and non-porous solid scintillator, such as paints of inorganic phosphors (e.g. doped zinc sulphide paint).

The monitor 5 illustrated in Fig.2 is of similar geometry to the monitor of fig. 1 except that the gas 6 passes through a porous hygroscopic scintillator element 7, for example a porous powder compact supported on a filter 8. In this case, the amount of

hygroscopic material applied to the powder compact should be limited, not to block the passage of the test gas. The light pulses emitted from the scintillator element 7 reach the light detector 9.

The monitor 10 illustrated in Figure 3 comprises a simple geometry with high light collection efficiency which is achieved by coating a thin layer of solid scintillator material 11 onto the face of a light guide 12, before applying the hygroscopic layer. Even more simply, it is possible to eliminate the light guide 12, applying the solid scintillator directly onto the face of the light detector 13.

Fig.4 illustrates a monitor 20 comprising parallel sheets of solid scintillator (e.g. plastic, glass, scintillating crystal) 21, having the hygroscopic layer coated thereon, and glued (using transparent glue) inside a channel 22 traversing a light guide 23. The same overall geometry may be realized by making the sheets from the light-guide material, and then coating them with a layer of solid scintillator, before applying the hygroscopic layer.

The overall geometry shown in fig.4 can alternatively be obtained by making it from a single block of plastic or resin: e.g. by injection moulding which can act as a light guide. The surfaces of the parallel plates are then coated first with a solid scintillator and then with a hygroscopic layer.

In monitor 30 illustrated in figure 5, solid scintillator fibres 31 are coated with the hygroscopic layer and held in a tube 32: the fibres themselves acting as light guides. The same geometry can be obtained by first coating non-scintillating transparent fibres with a layer of solid scintillator.

Figure 6 illustrates a monitor 40 a single light-detector 44 with a spiral of hygroscopically-coated plastic scintillator sheet 41 glued onto the end-plate of the light guide 42, which forces the gas to spiral inwards towards the central outlet tube (reverse flow is also possible). Fig.7 shows a similar hygroscopically coated scintillator element, this time with axial gas flow and no light guide.

Figures 4,5 and 7 show double light detectors, to enable background noise reduction by coincidence detection. In each case, one of the two detectors can be replaced by a reflector if pulse coincidence detection is not desired. Conversely, in the other designs, two light detectors may be used instead of one to allow pulse coincidence detection: they can both view the same side of the hygroscopic scintillator element where it is not advantageous to mount the detectors on opposite sides (e.g. if the scintillator is opaque).

Prototype monitors and initial results

To be of use, the monitor must have a limit-of-detection for HTO below the limit set by the International Commission on Radiation Protection for the HTO concentration in air which may be breathed by workers. This value is the derived air concentration (DAC), and equals 8×10^5 Bq/m3.

Two monitors were constructed using hygroscopically-coated plastic scintillator in sheet form. The geometries of the monitors corresponded to those illustrated in fig.4 and fig. 6. After forming the scintillator sheet into a spiral (fig. 6) or gluing the sheets in position (fig.4), the surface of the plastic scintillator material was treated with non-ionic detergent, dried in air, painted with a layer of

zinc chloride solution, and the excess blown off with compressed air. By varying the concentration of the zinc chloride (a strongly deliquescent salt) it was possible to produce a continuous solution layer about 1 micron thick, in equilibrium with the humidity of room air. This was found to be about the optimum thickness for giving a combination of good sensitivity and fast response to changing HTO concentrations in the passing gas.

Subsequently, a third prototype monitor was made using the geometry illustrated in fig 2. In this case the scintillator element 7 was made using a compacted layer of YAP powder mounted on a glass-fibre filter. This was wetted with detergent, dried and then a certain amount of zinc chloride solution was uniformly applied to render it hygroscopic; in the first tests 2mg of solution was applied (weighed when in equilibrium with ambient air at 58% relative humidity).

Air loaded with 30% relative humidity of either plain water vapour or tritiated water vapour was passed through the monitors according to the invention at 3 litres/minute.

All monitors showed sensitivities to HTO better than 0.1 DAC . If inlet air containing plain water vapour was substituted by air containing tritiated water vapour, 50% of the final value was reached in less than 1 minute. The time response results were roughly what one would expect on the basis of complete mixing between the HTO in the passing air with the water in the zinc chloride solution. This conclusion was confirmed by tests which showed that the response time was inversely proportional to the flow rate.

Tests were subsequently conducted with various loadings of zinc chloride solution and with various relative humidities in the test gas. The effect of changing relative humidity, for a given HTO activity in the test gas, depended on the detector geometry and the amount of zinc chloride applied. Tests using a thickness of zinc chloride about 0.4 microns (at 60% r.h.) showed the least change in sensitivity with relative humidity.

There was a slight tendency for the monitors using plastic scintillator to reduce in sensitivity with time: this was ascribed to the redistribution of the deliquescent salt layer so as to make it less uniform in thickness. The effect was reduced by replacing the zinc sulphate solution by a polymeric gel of zinc sulphate solution.